Original Research Article

Preparation and Characterization of Phthaloyl Chitosan As a Novel Purifying Agent for Deltamethrin

Abstract

For the development of a bio adsorbent with enhanced adsorption properties to remove deltamethrin pesticide from aqueous solutions, a modified chitosan material was successfully obtained by crosslinking chitosan with phthalic anhydride. The obtained products were characterized with the necessary chemical and spectroscopic techniques and were studied as an adsorbent for deltamethrin removal from aqueous solutions. For the determination of the optimum conditions of this reaction, pH, the initial dose of deltamethrin and the amount of modified chitosan to be added were mentioned. The decrease in the concentration of the previously prepared sample due to the adsorption reaction was studied with the aid of gas chromatography.

Keywords:
Chitosan, Pesticide, Chemical modification, Nanoparticles, Polysaccharide, Deltamethrin

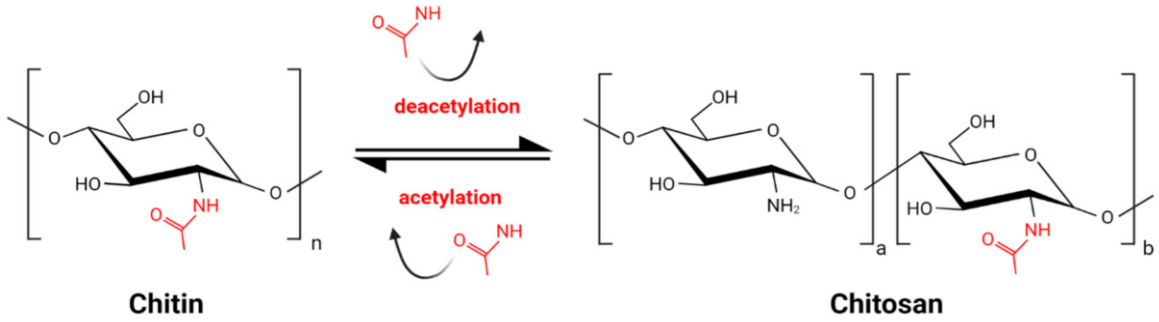
1. Introduction

Chitosan has gained great importance in biomaterials formulation because of its outstanding biological capabilities and has been extensively investigated in drug delivery systems. Chitosan is biocompatible and biodegradable to a high degree. Other important qualities include hemostatic, bacteriostatic, anti-cholesterics, anticarcinogenic, and fungistatic capabilities [1].

Chitosan is a type of natural green polymer but on the other hand, it is water-insoluble, and acid resistant, because of these limitations, its pure use is frequently limited. It is vital to change chitosan to maximize the utilization of chitosan resources while also broadening its application range. Improving chitosan solubility by chemical modification is a viable option. It may also increase chitosan's physicochemical properties, such as thermal stability, rheological properties, oxidation resistance, and antibacterial capabilities, at the same time. As a result, chitosan's applications are becoming more diverse [2].

Chitosan can obtain chitosan through the deacetylation of chitin. see scheme 1., the molecular structure of chitosan has three types of active groups: amino groups, primary and secondary hydroxyl groups at the C-3 and C-6 locations, which allow chitosan to undergo chemical modification reactions. The primary hydroxyl group, C6-OH, has a small steric hindrance, whereas the secondary hydroxyl group, C3-OH, has a large steric hindrance. As a result, the primary hydroxyl group may spin freely while the secondary hydroxyl group cannot.

The amino group is often more reactive than the primary hydroxyl group, and the primary hydroxyl group is more reactive than the secondary hydroxyl group. So, the chemical modification can be produced by N-modified, O-modified, or N, O-modified chitosan derivatives [3],[4].



Scheme 1. Deacetylation of Chitin to produce Chitosan

Conjugation of chitosan with other compounds is a smart carrier system that has been studied, the conjugation of chitosan and folic acid or glucose is an example of this type [5],[6]. Folate receptor is known as a highly specific tumor marker, commonly over-expressed in cancer tumors [7]. Huijuan et al. [8] succeeded in preparing folate chitosan conjugate nanoparticles with Doxorubicin hydrochloride (DOX), an anthracycline and effective anticancer drug, that has been widely used in chemotherapy for the treatment of various cancers, the prepared formula does not exhibit any cell toxicity and improves the cell uptake capacity of the drug due to the folate-receptor mediated endocytosis [9].

Chitosan could react with fatty aldehydes and aromatic aldehydes/ketones in a neutral medium to form Schiff bases. This reaction is extremely beneficial for chitosan research and use., the reaction might be employed to protect the amino group on the chitosan, allowing the reaction to occur on the hydroxyl group, and the protective group to be removed with an acid

when the reaction is completed. The Schiff base generated from the reaction of aldehyde with chitosan might be reduced by sodium borohydride to produce several specific-purpose chitosan N-derivatives [10]. The N-carboxymethyl chitosan, which is readily soluble in acid and alkali solutions is the result of the interaction between glyoxylic acid and chitosan [11].

The purpose of carboxylation is to insert acidic groups into the main chain of chitosan to increase the product's solubility, moisturizing, and film-forming capabilities and broaden its range of applications. Currently, carboxy methylation is the primary method used to study the carboxylation reactions of chitosan. The substitution order of carboxymethyl is C6- OH > C3-OH > C2-NH_2. N-carboxymethylation, O carboxymethylation, or N, O-carboxymethylation chitosan could be prepared through different reaction conditions and reagents. For obtaining O-carboxymethylated chitosan derivatives the reaction occurs in the presence of monochloroacetic acid and sodium hydroxide with isopropanol/water as a solvent at room temperature or in an ice bath. If the targeted derivative is N-carboxy methylation and N, O- carboxymethylation the reaction occurs when temperature rises. In addition, N-carboxymethylated products could also be obtained by direct alkylation [12],[13].

Cross-linking technology is a common method to improve the structural stability and mechanical properties of CS. By using a cross-linking agent (glutaraldehyde (GLA) [14], epichlorohydrin (ECH) [14, 15], tripolyphosphate (TPP) [16], ethylene glycol diglyceryl ether (EGDE) [17], polyethylene glycol (PEG) [18], genipin, ethylenediamine [19, 20], silane coupling agent [21] and diethylenetriaminepentaacetic.

Synthetic insecticides like deltamethrin are commonly employed in agriculture because of their exceptional efficacy in eliminating a variety of insects. However, when released from treated wastewater, deltamethrin can negatively impact aquatic ecosystems, therefore, in order to avoid any detrimental effects on the environment, wastewater must be treated to eliminate deltamethrin before it is released [22].

2. Experimental

2.1 Materials

Chitosan was obtained from San Huan Ocean Biochemical Co. Ltd. (China). Its degree of deacetylation and the apparent viscosity were determined as 91.2% and 30 MPa s. PVA was purchased from Sigma Aldrich. N, N-dimethylformamide (DMF) was dried over magnesium sulfate and purified by distillation. Phthalic anhydride was of reagent grade and used as received. Potassium bromide (KBr) (FTIR grade, ≥ 99% trace metals basis) was obtained from Lonza, Switzerland. CO_2 incubator (Heracell incubator, Thermo Scientific, USA). Acetone (2 propanone) HPLC grade. Most of the other chemicals and materials were stored in well-controlled storage conditions including ventilation, humidity, and temperature.

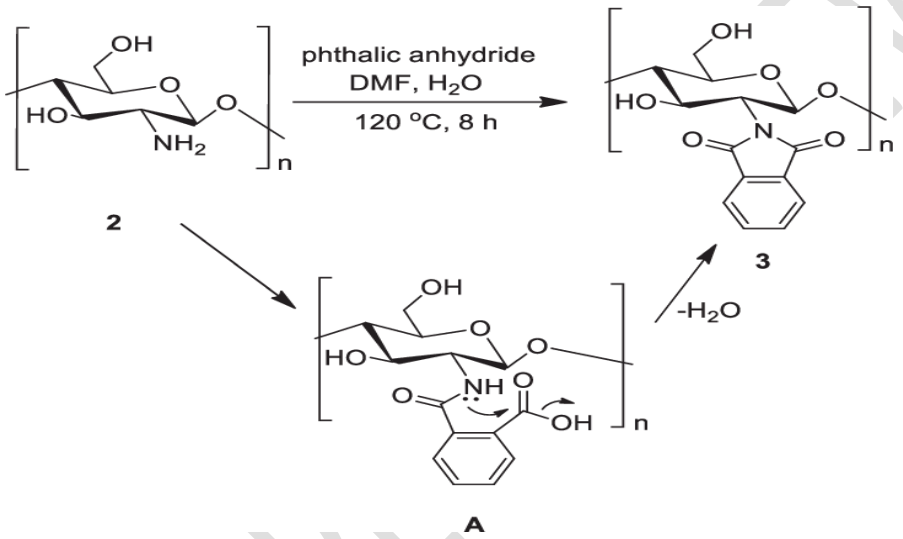
2.2 Preparation of Phthaloyl Chitosan Nanoparticles

In a three-necked flask a solution of 4.15 g of phthalic anhydride in 30 mL of N, N dimethylformamide (DMF) containing 5% (v/v) water was added, 1.5 g of fully deacetylated chitosan, the mixture was heated in nitrogen at 120 ^{0}C with stirring as the reflux system represented in Fig. 1

Fig. 1 Reflux system for phthaloylation reaction of chitosan

After 8 h of reaction, the resulting pale tan mixture was cooled to room temperature and poured into ice water. The precipitate was collected on a filter paper, washed with 150 mL of methanol at room temperature for 1 h, and dried to give 2.22 g of the product as a pale tan powdery material see Fig. 2 and Scheme 2.

Fig. 2 Wet pale tan paste resulted from the phthaloylation reaction of chitosan



Scheme 2. Phthaloylation of chitosan by phthalic anhydride/DMF, H_2O

3. Results and Discussion

3.1 Particle Size and Zeta Potential Measurement

5 mg of pure chitosan and phthaloyl chitosan was suspended in 1 ml of 1% acetic acid solution (pH 4.5 was adjusted by NaOH) before measurement. The prepared particles were analyzed for their particle size and size distribution in terms of the average volume diameters and polydispersity index by photon correlation spectroscopy using particle size analyzer Dynamic Light Scattering (DLS) (Zetasizer Nano ZN, Malvern Panalytical Ltd, United Kingdom) at fixed angle of 173° at 25° C. Samples were analyzed in triplicate. The same equipment was used for the determination of zeta potential, shown in Table 1.

Table. 1. Particle size and Zeta potential for pure chitosan sample and phthaloyl chitosan

Sample	Tested	Test	Unit
Pure Chitosan	Particle size	2078 ±	nm
	PDI	0.9 ± 0.15	
	Zeta potential	31.1 ±	mV
Phthaloyl Chitosan	Particle size	1162 ±	nm
	PDI	0.72 ±	
	Zeta potential	45.3 ±	mV

3.2 FTIR of Pure Chitosan and Phthaloyl Chitosan

In this work, we forward like to improve the solubility of chitosan, the structure of chitosan was modified to produce N-phthaloyl chitosan. Introducing the bulky phthaloyl group to the chitosan backbone will enhance the hydrophobicity character of chitosan and improve the solubility in organic solvents. This result may be referred to as the prevention of inter and intra-hydrogen bond formation. The FTIR spectrum of phthaloyl chitosan showed bands at 1622 cm^{-1} and 1413 cm−1 representing the phthalimido groups, which can act as complexation sites. The phthalimido group has therefore substituted the amino group of chitosan completely. For chitosan, the absorption at around 3448 cm^{-1} was assigned to the stretching vibration of –OH and –NH2. The band at around 1712 cm^{-1} was assigned to the bending vibration of $–NH_2$. Two strong absorption bands at around 1386 and 1056 cm^{-1} were related to the C–O stretching vibration of the second hydroxyl group and primary hydroxyl group, respectively. The spectra of N-phthaloyl-chitosan showed two strong characteristic absorptions at 1072 cm^{-1}, which were assigned to the stretching vibration of C=O. shown in Fig. 3 and Fig. 4.

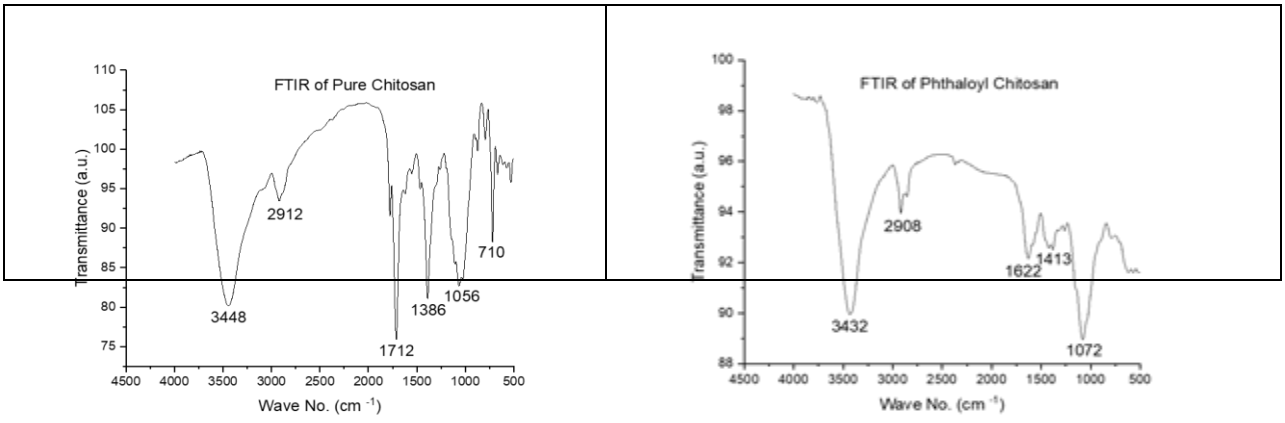


Fig. 3 FTIR spectra of Pure Chitosan	Fig. 4 FTIR spectra of Phthaloyl Chitosan

3.3 Scanning Electron Microscopy (SEM) Characterization

The morphology of phthaloyl chitosan was studied by SEM Fig. 5, by studying images with different magnifications at different areas of samples. The SEM images of phthaloyl chitosan exhibited a semi-spherical surface and showed a heterogeneous porous structure and a compact morphology. It was found that in some areas there is a difference in size and shape.

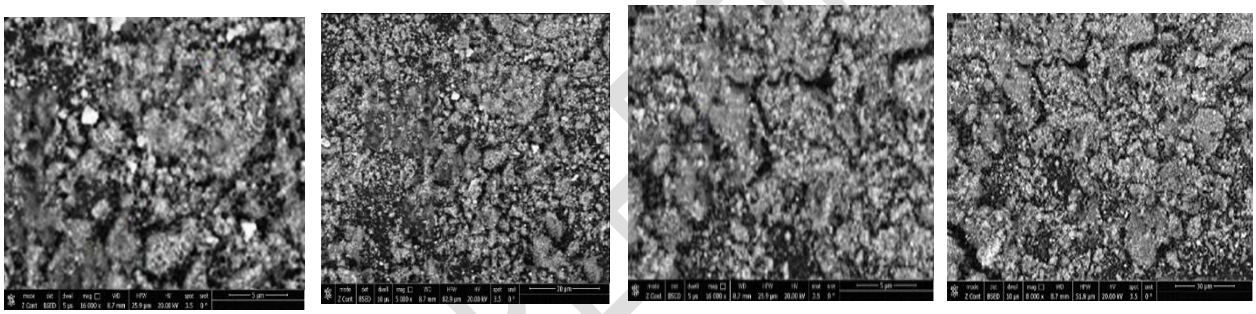


Fig. 5 SEM images of phthaloyl chitosan

3.4 Adsorption Efficiency of Phthaloyl Chitosan for Deltamethrin as an Application

In this part, we use a Gas chromatography instrument to prove that there is an effective feature of modified chitosan as an adsorber for some pyrethroid pesticides such as deltamethrin which is considered a popular insecticide around the world. Deltamethrin is a pyrethroid ester insecticide. Deltamethrin plays a key role in controlling malaria vectors and is used in the manufacture of long-lasting insecticidal mosquito nets; however, the resistance of mosquitos and bed bugs to deltamethrin has seen a widespread increase. Deltamethrin is toxic to aquatic life, particularly fish. Although generally considered safe to use around humans, it is still neurotoxic. It is an allergen and causes asthma in some people. From this point of view, there is a persistent need to find effective, safe, and economical ways to control and reduce the hazards of the

chemical compounds that we consume in a routine pattern. By using the gas chromatography analysis method, we will study one of the promising applications of chitosan as an adsorber for pesticides and controlling agents. The method used for analysis is validated by examining different validation items, such as repeatability, linearity, limit of quantification, and detection.

The instrumental method used in this part are validated method, by using GC capillary column 30 m X 0.25 mm with RTX-5 AMINE (cross bond 5 % diphenyl/95 % dimethyl polysiloxane) with temperature 280 0C, the detector is FID type and its temperature is 300 0C, the injector part (inlet) temperature is 290 0Cm the carrier gas is helium with flow rate 2.2 ml/min, also the nitrogen can be used as a carrier gas but the flow rate must be modified to get suitable peaks shape. Helium is better than nitrogen as a carrier gas due to its high-resolution peaks and low noise in the baseline.

We start by preparing 0.06 % (w/w) of deltamethrin as a trial product by mixing it with talc powder then we divide the mixture into three equal batches named respectively B1, B2, and B3, the three batches are brought into a reaction with three different weights of modified phthalate chitosan 5.4, 7.8 and 11.4 mg respectively and complete the volume by acetone and stirring for 8 hours and sonicate for 15 minutes. Each flask is filtered by Millipore filters to remove the non-soluble chitosan before injection by GC. By altering the pH of the prepared solution at pH = 4.7 and pH = 8.1 we can make a clear understanding of the pH effect on the adsorption reaction, the chromatogram and discussion about the results are tabulated below. For each batch, the following injection order was carried out STD, 5.4 mg Ph-CS, 7.8 mg Ph-CS, 11.4 mg Ph-CS, pH 4.7 and pH 8.1 by adding dropwise 10 % sodium hydroxide solution. The equation used for calculation the concentration is given:

$$\text{C (w/w) \%} = \frac{SPL\,(area)}{STD\,(area)} \times \frac{STD\,(wt)}{SPL\,(wt)} \times 100\ \%$$

Where: SPL (area): Area from sample injection, STD (area): Area from standard injection, STD (wt): weight of pure standard, SPL (wt): Weight of sample. The following three tables represent the chromatography data of the three batches (B1), (B2) and (B3) respectively:

Table 2: Chromatography data of batch B1

B1	Weight (mg)	Rt (min)	Area mV*s	Concentration (w/w) %	SD σ
STD	14.64	5.80	211.43	100 %	-
5.4 mg Ph-CS	18505.7	5.80	148.59	0.0556	
7.8 mg Ph-CS	19254.9	5.79	132.35	0.0553	0.000169
11.4 mg Ph-CS	19375.7	5.77	151.27	0.0552	
pH 4.7	18505.7	5.80	147.68	0.0553	-
pH 8.1	18505.7	5.80	148.09	0.0554	-

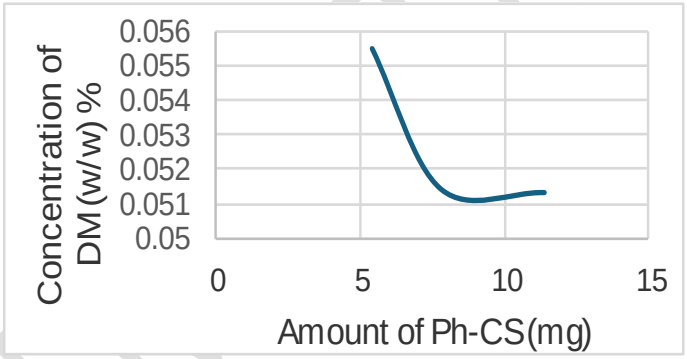


Chart 1. Relation between the amount of Ph-CS added and the concentration of DM for Batch 1

Table 3:

B2	Weight (mg)	Rt (min)	Area mV*s	Concentration (w/w) %	SD σ
STD	14.64	5.80	215.16	100 %	-
5.4 mg Ph-CS	18498.8	5.80	150.89	0.0555	
7.8 mg Ph-CS	19390.9	5.78	138.61	0.0514	0.00195
11.4 mg Ph-CS	19278.7	5.81	127.54	0.0513	
pH 4.7	18498.8	5.80	151.60	0.0558	-
pH 8.1	18498.8	5.80	150.29	0.0553	-

Chromatography data of batch B2

Table 3: Chromatography data of batch B2

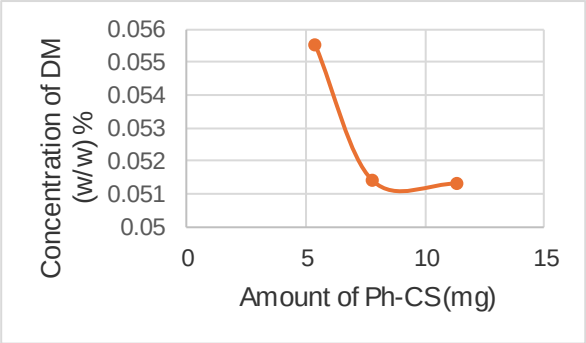


Chart 2. Relation between the amount of Ph-CS added and the concentration of DM for Batch 2

Table 4: Chromatography data of batch B3

B3	Weight (mg)	Rt (min)	Area mV*s	Concentration (w/w) %	SD σ
STD	14.64	5.80	215.45	100	-
5.4 mg Ph-CS	18556.9	5.81	151.97	0.0556	0.000571
7.8 mg Ph-CS	19299.7	5.80	142.44	0.0545	
11.4 mg Ph-CS	18978.8	5.78	147.42	0.0543	
pH 4.7	18556.9	5.81	150.89	0.0552	-
pH 8.1	18556.9	5.81	151.31	0.0554	-

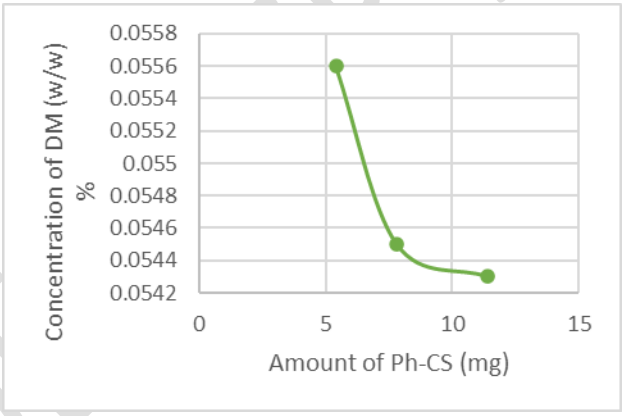


Chart 3. Relation between the amount of Ph-CS added and the concentration of DM for Batch 3

4. Conclusion

The accelerated development of polymer chemistry enables this science to contribute in different applications aspects, in this work we successfully prepared and modified the backbone of the chitosan polymer as initial step for preparation of drug carriers. The key point of this success can be referred to wide and diversity possibility of making an modification on the polymer material in order to enhance the chemical and physical properties of the material and make it more appropriate for the demanded application. We success to prepare the modified

grafted derivative of chitosan by phthaloylation reaction and gave a clear characterization study for the prepared derivative. The prepared modified chitosan derivatives show a potential power for using this novel drug carrier in pesticide clarification processes and controlling the hazards of such chemical compounds.

5. References

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